HIGH-TEMPERATURE COBALT-TUNGSTEN ALLOYS

FOR AEROSPACE APPLICATIONS

by John C. Freche, Richard L. Ashbrook and Gary D. Sandrock | [19637

NASA. Lewis Research Center) Cleveland, Ohio

SUMMARY

11900 over

An investigation was conducted to extend the high-temperature capability and workability of cobalt-tungsten alloys for aerospace applica-The average life at 1850° F and 15,000 psi of the strongest previously reported alloy Co-25W-lTi-lZr-0.4C was doubled from 92 to 185 hours by small additions of chromium and rhenium. At 2200° F and 5000 psi the strongest alloy, Co-25W-lTi-lZr-3Cr-2Re-0.4C, had a rupture life of 23 hours. The elevated temperature rupture strength of this alloy compared favorably with the strongest available conventional (high chromium) cobalt-base alloys. Above approximately 2035° F and at reasonably high stress levels (10,000 and 15,000 psi) its stress rupture life also exceeded those of the strongest known nickel-base alloys, including the NASA tantalum-modified alloy and SM-200.

It is particularly significant that even the strongest alloys of this series were readily hot-rolled. Ingots 1/2-inch thick were reduced to 0.065-inch sheet and subsequently cold-rolled to 0.0125-inch sheet. Elongations as high as 31 percent were obtained at room temperature with annealed sheet specimens. The good ductility obtained suggests that these



alloys could be fabricated into complex shapes required for various aerospace and other applications.

Elevated temperature tensile strengths of annealed sheet of the strongest chromium—and rhenium—modified alloys were approximately the same as for the cast alloys. The elongation of the wrought material was substantially greater, however, with an average elongation of 35 percent at 1800° F. At room temperature these alloys had tensile strengths above 210,000 psi and elongations above 25 percent in the as-rolled condition.

Although the strongest alloys had a chromium content of only 3 percent, they did not oxidize catastrophically in air. When they were coated with a commercial aluminum-iron coating, oxidation in 300 hours at 1900° F was negligible. \mathcal{R} $\mathcal{I} + \mathcal{H} o \mathcal{R}$

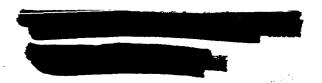
INTRODUCTION

In view of the potential of cobalt-tungsten alloys for a variety of aerospace and other high-temperature applications, the investigation of a series of these alloys has continued at the NASA Lewis Research Center to extend further their high-temperature capability and at the same time to retain or to improve their workability characteristics. Earlier investigations have indicated that cobalt-tungsten alloys are particularly promising for achieving high-temperature strength (refs. 1 and 2). The authors have shown that a Co-25W-1Ti-0.4C alloy and a Co-25W-1Ti-1Zr-0.4C alloy had stress-rupture properties in air that compared favorably with such conventional cobalt-base alloys as SM-302 and



WI-52 (ref. 3). In addition, these alloys had high ductility and could readily be rolled into sheet. Although the cobalt-tungsten alloys described in reference 3 would not be expected to have the excellent oxidation resistance of chromium- and aluminum-bearing superalloys, they did not oxidize catastrophically at high temperatures. On the contrary, their long stress-rupture lives in air indicated that they should have at least limited applicability in an air environment. Also, the use of coatings, which is now widely considered for superalloys in many high-temperature applications such as turbine stator vanes and turbine buckets, indicates an enhanced potential for these alloys.

Another possible area of interest for these alloys is space-powersystem applications. In the vacuum environment of space, oxidation resistance, of course, is not a requirement. One of the promising advanced space power systems under development is the turboelectric system
illustrated schematically in figure 1, in which nuclear power is converted to electrical power by means of a closed thermodynamic cycle of
either the Rankine or Brayton type (ref. 4). Certain components of such
a system, namely, the radiator, ducting, and various turbogenerator components, function at temperatures and stresses for which cobalt- and
nickel-base superalloys are particularly well suited. Cobalt-base alloys
have several important advantages over nickel-base alloys for such applications. The higher melting point of cobalt indicates a potential for
use at higher temperatures. Resistance to liquid-metal corrosion is an
important consideration in electric propulsion systems where the ducting,



radiator, and turbine components are continuously exposed to a liquid metal heat-transfer fluid, which is the case when the Rankine cycle is used. Cobalt-base alloys appear to have better resistance to corrosion by mercury than do nickel-base and certain iron-base alloys, although they are inferior to refractory metals (ref. 5). Extensive research is still required, however, to establish fully the performance of cobaltbase and other alloys in alkali-metal environments. Corrosion, of course, would not be a problem if an inert gas were used as the heattransfer fluid, as in the Brayton cycle (ref. 4), although in this case the possibility of carbon depletion or contamination by traces of oxygen or nitrogen cannot be overlooked. Finally, cobalt has a lower evaporative loss rate than either nickel or iron. Tungsten, the major alloying element in the alloys of this investigation, has an even lower evaporative loss rate (ref. 6). Low evaporative loss rates are important in order to reduce the possibility of structural deterioration due to evaporation upon long-time (10,000- to 30,000-hr) exposure at elevated temperature to the high vacuum environment of space.

Because of the advantages afforded by cobalt-tungsten alloys, investigation of these materials was continued. This paper presents the results of systematic alloying studies based on the strongest cobalt-tungsten alloy, Co-25W-lTi-lZr-0.4C, previously reported by the authors (ref. 3). High-temperature strength properties of the strongest alloy developed in the present investigation were determined up to 2200° F. Rollability of the stronger alloys as well as the 1900° F oxidation resistance of selected alloys was also investigated. Comparisons with the strongest conventional (high-chromium) cobalt-base alloys are presented.

The state of the s

EXPERIMENTAL PROCEDURE

Alloys Investigated

The strongest previously developed alloy in this series,

Co-25W-lTi-lZr-0.4C, was modified by systematic additions of chromium

and rhenium. Chromium was considered because it has been shown to be

one of the most effective elements for strengthening the binary alloy

Co-25W (ref. 2). Rhenium was considered as a potential solid-solution

strengthener.

Chromium, of course, is a highly volatile metal, and its presence in an alloy that might be used in space-vehicle components could be detrimental. The calculated evaporation losses in vacuum of various metals, including chromium, are shown in figure 2 in inches per 10,000 hours as a function of temperature. These data were compiled from reference 6. It is evident from the figure that chromium is one of the more volatile metals, and this consideration led to the use of only low volatility alloying constituents in the earlier alloys of this series. Although chromium has a high evaporation rate, it might reasonably be expected, however, that its presence in relatively small amounts in alloys would not be as detrimental insofar as evaporation loss is concerned, as would the relatively large amounts (20 to 25 percent) present in conventional cobalt-base alloys (table I). If present in small quantities, the concentration of chromium at the surface would be less, as would the concentration gradient, and consequently the driving force for diffusion of chromium to the surface would be less.

In the process of investigating the effect of chromium additions on alloy strength, emphasis was placed upon small chromium additions up to 5 weight percent (6.64 atomic percent).

The evaporative loss rate of rhenium, the other alloying addition considered, is extremely low, and falls off the scale to the right of figure 2. Because of its high cost, rhenium additions greater than 3 percent (1.14 atomic percent) were not investigated. The compositions of all the alloys investigated are shown in table I. All alloy additions were made by adjusting (i.e., subtracting from) the cobalt content.

<u>Purity of raw materials.</u> - The purities of the alloying elements used, as reported by the suppliers, were as follows:

Element	Purity, weight percent
Co	99.5+
Ti	99.3+
W	99.9+
Zr	99.9+
Cr	99.5+
Re	99.9+
C	99.5+

Chemical analysis. - Representative heats of the compositions investigated were chemically analyzed by an independent laboratory. Table I shows the results of these analyses. Some losses in the charging elements were observed. These losses might be expected for relatively high vapor pressure elements such as chromium, or highly reactive elements such as

zirconium. The greatest variation from the nominal composition occurred as the result of the loss of zirconium. About one-half of the l percent zirconium addition was retained.

Casting and Inspection Techniques

The casting procedure was similar to that used in the initial phase of the investigation (ref. 3) and in nickel-base alloying studies made at the NASA (refs. 7 and 8). A 50-kilowatt, 10,000-cps water-cooled induction unit was used in melting. All melts were made in stabilized zirconia crucibles under a blanket of commercially pure argon. The raw materials for the melts were electrolytic cobalt and chromium, ground tungsten rod, powdered rhenium, sponge titanium and zirconium, and carbon black, which was briquetted before charging. Pouring temperature, as read by an optical pyrometer and corrected for the low emissivity of the melt, was $3100^{\circ}\pm50^{\circ}$ F. The castings were poured statically, without argon protection, into silica investment molds heated to 1600° F. Molds were allowed to cool overnight before the investment was removed from the castings.

The lost-wax process was used to make molds for stress-rupture - and tensile-test specimens. The same design of specimens was used for both stress-rupture and tensile tests of as-cast material. These specimens have conical shoulders with a 20° included angle. The gage section was $1\frac{3}{8}$ inches long and 1/4 inch in diameter. All castings were radiographed and then inspected either with fluorescent penetrant dye or visually at a magnification of 10.

Blanks for rolling studies were cast into a copper chill mold that provided a slab $\frac{1}{2}$ by $1\frac{3}{4}$ by $2\frac{1}{2}$ inches after the riser was removed.

Rolling

Before rolling, the chill-cast slabs were machined to remove surface imperfections. The machined thickness varied from 0.475 to 0.495 inch. These slabs were unidirectionally rolled at 2150° F. Reductions of 0.020 to 0.025 inch per pass were made until strips approximately 18 by 2 by 0.065 inches were obtained. Tensile specimens having a test section 1 inch long by 0.175 by 0.050 inch were machined from these strips.

In order to determine the feasibility of obtaining ultrathin sheet, sections of 0.065-inch hot-rolled strip were further reduced by cold rolling in approximately 1/2-mil passes to a final thickness of 0.0125 inch, the practical limit of the rolls. Intermediate anneals of 1/2 to 3 minutes (depending on section thickness) at 2150° F followed by air cooling to room temperature were performed after each 10 passes (5-mil reduction). Annealing was done in an air atmosphere. Figure 3 illustrates a chill-cast slab, a 0.065-inch hot-rolled strip, and an annealed 0.0125-inch strip of alloy Co-25W-1Ti-1Zr-3Cr-2Re-0.4C. The 0.0125-inch sample was heat treated for 10 minutes at 2150° F in an argon - 2 percent hydrogen atmosphere before being bent into the Z-shape shown. A protective atmosphere was employed in the longer post-rolling annealing treatment in order to prevent formation of external scale and internal oxidation.

Protective Coatings

A limited number of as-cast oxidation and stress-rupture specimens were coated in order to determine the degree of improvement in oxidation resistance and rupture life that might be obtained. A proprietary aluminum-iron diffusion coating was applied in a pack treatment by Union Carbide Stellite Co.

Alloy Evaluation

Stress-rupture and tensile tests. - Table II shows the alloys and conditions of operation for stress-rupture testing. All of the alloys were tested in the as-cast condition without protective coatings. In addition, two of the alloys were provided with protective coatings and limited stress-rupture data were obtained. Table III shows the alloys and conditions of test for tensile tests. All tensile tests were run in air. Sheet specimens were tested in the as-rolled and in a heat-treated condition. The heat treatment consisted of a 1/2-hour anneal at 2350° F in argon that contained 2 percent hydrogen to prevent oxidation, followed by a water quench.

Hardness. - Rockwell C hardness measurements were made on coupons cast along with the test bars of the experimental alloys investigated.

An average of at least five readings was taken as representative of the hardness of each alloy.

Oxidation. - A large (20 cu ft) resistance-wound hearth-type furnace was used to determine oxidation behavior of selected alloys. Cylindrical specimens, approximately 0.225 inch in diameter and 0.875 inch long, were

machined from cast test bars of the alloys investigated. Such specimens were suspended by means of platinum wires spotwelded to one end.

Furnace temperature was maintained at 1900° F. One specimen of each alloy was removed after particular time increments during the test.

The weight gain, including any spalled oxide, was determined per unit of original surface area for each individual specimen.

Metallographic examination. - The more promising alloys were examined metallographically in the as-cast, as-rolled, and heat-treated conditions. Photomicrographs at magnifications of 250 and 750 are presented.

RESULTS AND DISCUSSION

Stress-Rupture Properties

The initial evaluation of these alloys was made in air to facilitate their development. Their ultimate evaluation for space-power use must be made by long-time tests in a vacuum environment. The data from the stress-rupture tests are summarized in table II. Figure 4 shows the effect of nominal chromium additions on the stress-rupture life of alloy Co-25W-1Ti-1Zr-0.4C at 1850° F and 15,000 psi. Straight lines connect the average life values obtained with each alloy. Additions of chromium of 3 to 5 weight percent (4 to 6.6 atomic percent) resulted in the greatest increases in life. Average lives of approximately 130 hours were obtained with both the 3- and the 5-percent alloys.

Since alloy Co-25W-1Ti-1Zr-3Cr-0.4C contained the lowest amount of chromium that was effective in increasing stress-rupture life, this alloy was selected for further alloying studies. The effect of nominal rhenium

additions on rupture life of this alloy at 1850° F and 15,000 psi is shown in figure 5. Substantial improvement in rupture life was achieved. The strongest alloy, which resulted from a 2-percent (0.76-atomic-percent) rhenium addition, had an average rupture life of 185 hours.

Figure 6 illustrates the as-cast stress-rupture properties of the 3 percent Cr modified alloy (fig. 6(a)) and the 3 percent Cr - 2 percent Re modified alloy (fig. 6(b)) at several temperatures. Lines (best visual fit) were drawn through the average life values obtained at each stress level with uncoated test specimens. It is significant that both alloys have long life over a wide range of stresses at temperatures up to 2000° F. The chromium-rhenium modified alloy was investigated up to 2200° F and even at this high temperature had good rupture properties. In the uncoated condition at this temperature, for example, this alloy had a rupture life of 23 hours at a stress of 5000 psi. Catastrophic oxidation clearly did not occur with either of these alloys in the unprotected condition even at the highest test temperatures. Limited data for coated test specimens are also shown. These data show that life was extended slightly by the coating. It should be noted, however, that other coatings may provide superior protection; this aspect remains to be investigated.

The 15,000-psi as-cast stress-rupture properties of these alloys are compared with those of the strongest conventional cobalt-base alloys in figure 7. Figure 7(a) compares the alloy Co-25W-lTi-lZr-3Cr-2Re-0.4C at 1850° F with two commonly used cobalt-base alloys, HS-31 (ref. 9) and WI-52 (ref. 10), at 1800° F. The latter temperature was the highest for

which data were available for the commercial alloys. Although the data for the 3 percent Cr - 2 percent Re modified alloy were obtained at a temperature 50° higher than for HS-31 and WI-52, it is evident that even at this higher temperature alloy Co-25W-1Ti-1Zr-3Cr-2Re-0.4C is stronger than the commercial alloys. Figure 7(b) provides a comparison at 2000° F with two of the most recent commercial cobalt-base alloys. The 3 percent Cr - 2 percent Re modified alloy shows marked improvement over SM-302 (ref. 11). At times less than 90 hours alloy Co-25W-1Ti-1Zr-3Cr-2Re-0.4C also had greater strength than SM-322 (ref. 12). At longer times the curves of the latter two alloys were nearly coincident. It is particularly significant that while comparing favorably in strength with commercial cast alloys, even the strongest alloys of the present investigation were readily workable.

Nickel-base superalloys generally have greater strength than cobalt-base alloys at temperatures up to about 2000° F. However, since the melting point of cobalt is higher than that of nickel, a crossover in elevated temperature strength might be expected with increasing temperature. Figure 8 shows a stress-rupture comparison at stress levels of 10,000 and 15,000 psi over a range of temperatures of the 3 percent Cr - 2 percent Re modified alloy, the strongest alloy of this series, and SM-200 (ref. 13), one of the strongest nickel-base superalloys. At 10,000 psi (fig. 8(a)) a crossover in the alloy curves occurs at about 2035° F and at 15,000 psi (fig. 8(b)) it occurs at 2020° F, with the 3 percent Cr - 2 percent Re modified alloy having longer lives above these temperatures. Comparisons such as these suggest that the 3 percent Cr - 2 percent Re modified alloy has strength advantages over the strongest

NASA tantalum modified nickel-base alloy (ref. 14) for short-time applications at reasonably high stress levels and temperatures above 2035° F.

Tensile Properties

Tensile properties of both the 3 percent Cr and the 3 percent Cr - 2 percent Re modified alloys in the as-cast and rolled conditions are listed in table III. Since these alloys were the strongest in stress-rupture tests, they were chosen for further investigation. Figures 9 and 10 present tensile properties plotted as a function of temperature. Curves were drawn only through the as-cast data values since only limited sheet data are available. The average as-cast room-temperature ultimate strength of the 3 percent Cr modified alloy (fig. 9) was 96,400 psi, and the average elongation was 2.9 percent. For the 3 percent Cr - 2 percent Re modified alloy (fig. 10) the average tensile strength was 98,050 psi, and the average elongation was 2.3 percent. These values were not substantially different from those obtained for the strongest previously reported alloy in this series, alloy Co-25W-1Ti-1Zr-0.4C, which had an as-cast ultimate strength of 98,580 psi and a 3.5 percent average elongation (ref. 3).

At 1600° F the ductility of the as-cast 3 percent Cr and the 3 percent Cr - 2 percent Re modified alloys was approximately the same as at room temperature. At 1800° F, however, the average elongation of each alloy increased substantially to 17.2 and 26.2 percent, respectively.

These large elongations were observed up to 2100° F, the maximum tensile test temperature. The high elevated-temperature ductility doubtless accounts for the ease with which these alloys were hot-rolled.

Sheet tensile data up to 1800° F are also shown in figures 9 and 10. In the annealed condition (1/2 hr at 2350° F and water quench) both alloys in sheet form show elevated-temperature tensile strengths virtually identical to those obtained in the as-cast condition. At 1800° F, the highest temperature for which sheet data were obtained, the average sheet tensile strengths for the 3 percent Cr and 3 percent Cr - 2 percent Re modified alloys were 37,100 and 37,200 psi, respectively, approximately the same as for the as-cast alloys. At room temperature these alloys had sheet tensile strengths in the annealed condition of 173,750 and 181,750 psi, which are almost twice as high as the as-cast values (table III). The very high as-hot-rolled room-temperature tensile strengths (up to 227,000 psi for the 3 percent Cr modified alloy) should be of considerable interest for room-temperature applications when high-strength sheet is required. Still higher ultimate tensile strengths are probably obtainable with these alloys by cold-rolling.

Increases in room-temperature ductility of approximately one order of magnitude over the as-cast condition were observed with the sheet material. At 1600° F the ductility of the sheet was appreciably less than at room temperature, yet greater than that of the cast material. At 1800° F the elongation of the sheet material for both alloys was approximately 35 percent.

Hardness

Hardness data are summarized in table IV. Listed values represent an average of five or more readings for each specimen. Rockwell C hardness values of the as-cast alloys ranged between 30.5 and 34.5. There was no significant trend of increasing hardness with either increasing chromium or rhenium content. In the as-rolled condition, the 3 percent Cr-modified alloy had a Rockwell C hardness of 48.5. That of the 3 percent Cr - 2 percent Re modified alloy was 50.5. After a 1/2 hour, 2350° F post-rolling annealing treatment, the hardness of these alloys was 40 and 39, respectively.

Workability

Rollability of the two strongest alloys, Co-25W-1Ti-1Zr-3Cr-0.4C and Co-25W-1Ti-1Zr-3Cr-2Re-0.4C was also investigated. Ingots of each alloy 1/2-inch thick were readily rolled to thicknesses of 0.065 inch at 2150° F. Virtually no edge cracking was observed. Both alloys were also cold-worked from 0.065-inch hot-rolled sheet to approximately 0.012-inch sheet in about 1/2 mil reductions. To prevent cracking, a brief anneal (1/2 to 3 min, depending on thickness) at 2150° F after each 5 mil reduction was employed. Oxide scale formed during annealing was removed by light sandblasting. Occasional edge cracks were noticed during cold-rolling. These were removed by grinding before the next pass. The ease with which the alloys were rolled, both hot and cold, and the substantial elongation of the sheet both at 1800° F and at room temperature, suggest that these alloys could be fabricated into shapes required

for various aerospace applications (i.e., jet engine tailpipe assemblies, space power system ducting, etc.).

Oxidation Resistance

Figure 11 shows the 1900° F oxidation behavior of several alloys in this series compared with unalloyed cobalt and with WI-52, a cast cobalt The data are presented base alloy that contains 21 percent chromium. on the basis of weight gain per unit initial area. The alloys that contain 3 percent chromium together with 1 and 3 percent rhenium show a slightly better oxidation resistance than the previously reported alloys of this series (ref. 3) and considerably better oxidation resistance than unalloyed cobalt. WI-52 has substantially greater resistance to oxidation than the alloys containing only 3 percent chromium, as might be expected. To obtain an indication of the improvement in oxidation resistance that might be achieved by means of protective coatings, the 3 percent Cr - 2 percent Re modified alloy was tested in the coated condi-The weight gain observed was negligible. A visual comparison of coated and uncoated specimens after various test times up to 300 hours at 1900° F is provided in figure 12. The coated specimens were of alloy Co-25W-lTi-lZr-3Cr-2Re-0.4C while the uncoated specimens were of the 3 percent Cr - 1 percent Re modified alloy. Since the difference in oxidation behavior between the alloys containing 1 and 3 percent rhenium was negligible (fig. 11), it is valid to so compare the coated 2 percent Re and the uncoated 1 percent Re modified alloy (fig. 12). The coated specimens changed very little in appearance during the entire test.

coated specimens progressively increased in diameter and the grain size of the oxide layer appeared to coarsen with time. The oxide layer remained intact while the specimens were exposed to the test temperature; this is also indicated by the parabolic oxidation curves of figure 11. On cooling, however, the oxide tended to crack. On the specimen that was exposed for 310 hours, the oxide scale spalled off during handling.

The aluminum-iron diffusion coating offered excellent protection for unstressed specimens. The coating, however, appears to have only limited ductility. When used on highly stressed specimens that elongated appreciably during stress-rupture testing, it was less effective in preventing oxidation. Once the substrate had elongated and the coating had cracked, oxidation was not inhibited.

Metallographic Examinations

Figure 13 shows the as-cast microstructures of alloy

Co-25W-lTi-lZr-0.4C, the 3 percent Cr modification, and the 3 percent Cr
2 percent Re modification of this alloy at magnifications of 250 and 750.

The structures are similar in that all three show an interdendritic carbide network. A major difference is the amount of precipitate present in the matrix of each alloy. The Co-25W-lTi-lZr-0.4C alloy has the least amount of precipitate, whereas the 3 percent Cr modified alloy appears to have the greatest amount. There is what appears to be a pronounced depletion zone in the matrix adjacent to the carbides in both the chromium and the chromium-rhenium modified alloys.

Figures 14(a) and (b) show the microstructures of the rolled alloy Co-25W-1Ti-1Zr-3Cr-0.4C before and after heat treatment. In the as-rolled condition there is some evidence of recrystallization. The minor phases are strung out in the direction of rolling. After heat treatment at 2350° F for 30 minutes the rolled alloy showed substantial recrystallization. Also an appreciable amount of the minor phases present was taken into solution.

The microstructures of alloy Co-25W-lTi-lZr-3Cr-2Re-0.4C as-rolled and after annealing are shown in figures 14(c) and (d). In the rolled condition, as in the cast condition, this alloy showed less matrix precipitate than the 3 percent Cr modified alloy. The amount of recrystallization was about the same. After a post-rolling annealing treatment at 2350° F for 30 minutes, an appreciable amount of the minor phases was taken into solution, but, as in the case of the 3 percent Cr modified alloy after rolling and a similar heat treatment, some were retained.

It is evident that the heat treatment employed at 2350° is not a complete solution treatment for these alloys but rather an anneal. Although considerable recrystallization occurred, the carbides and other precipitates were only partially taken into solution. It is suggested that other heat treatments be investigated in order to determine the most satisfactory heat treatment.

CONCLUDING REMARKS

Although much additional information must be obtained in order to describe fully the properties of this alloy series, the data presented indicate that these alloys have considerable potential for various

aerospace and other applications. The combination of excellent formability together with a degree of high-temperature strength, presently available only in the strongest cast cobalt-base alloys, suggests advantageous uses in such jet engine components as combustion chambers and tailpipe assemblies. Stator vanes are an additional important possible application. Advanced jet engine designs now call for coating protection on many high-temperature components. Since only a limited investigation was made of the beneficial effects of protective coatings on the cobalt-tungsten alloys of this series, further work is clearly warranted.

These alloys should also find application in space power systems where oxidation is not a primary concern. An important characteristic of these alloys for such applications is their potentially lower evaporation rate in vacuum. Cobalt has a lower evaporation rate than either nickel or iron, the base metals of competing alloy systems. Moreover, the strongest alloys of this series contain no more than 3 percent of the volatile element chromium, while virtually all conventional superalloys (cobalt as well as nickel base) contain high percentages of chromium (up to 25 percent) or of the even more volatile aluminum (up to 7 percent). In principle, the low-chromium cobalt-tungsten alloys should be less adversely affected than conventional superalloys by long-time exposure to vacuum at elevated temperatures. Further experimental work is indicated to investigate this aspect of the behavior of cobalt-tungsten alloys.

Additional research is also indicated to establish the cause of the drop in ductility observed in 1600° F tensile tests with these alloys. Embrittlement due to aging may be the cause, and this must be investigated,

as must the degree to which mechanical properties are affected. The potential benefits of heat treatments insofar as improving the strength and/or ductility of these alloys is concerned should be explored. The high Curie temperature of cobalt (2066° F) together with the demonstrated high-temperature strength of cobalt-tungsten alloys would suggest that research also be directed toward developing their magnetic properties for electric generator applications. Finally, further alloying studies would appear to be warranted to extend the high-temperature strength of this alloy series.

SUMMARY OF RESULTS

The following major results were obtained from this investigation to extend the high-temperature capability and workability of cobalt-tungsten alloys for aerospace applications:

- 1. Small additions of Cr (3 percent) and Re (2 percent) to the strongest previously reported alloy in this series, Co-25W-1Ti-1Zr-0.4C, resulted in substantial improvements in high-temperature rupture strength. Average rupture life was doubled from 92 hours to 185 hours at 1850° F and 15,000 psi. At 2200° F, the highest temperature considered, and 5000 psi, the 3 percent Cr 2 percent Re modified alloy had a rupture life of 23 hours.
- 2. The 3 percent Cr 2 percent Re modified alloy compares favorably in elevated temperature rupture strength with the strongest available conventional (high chromium) cobalt-base alloys. Above 2035° F at high stress levels (10,000 and 15,000 psi) its stress rupture life also exceeded

those of some of the strongest know nickel-base alloys, including the NASA tantalum modified alloy and SM-200.

- 3. It is particularly significant that while comparing favorably in strength with commercial cast alloys, both the strongest chromium and chromium-rhenium modified alloys were readily hot-rolled from 1/2-inch-thick ingots to 0.065-inch sheet and subsequently cold-rolled to 0.0125-inch sheet. Maximum elongations of 23 and 31 percent, respectively, were obtained in room-temperature tensile tests with annealed sheet specimens of these alloys. These results suggest that these alloys could be fabricated into shapes required for ducting and radiator components for advanced space power systems.
- 4. The elevated temperature tensile strengths of annealed sheet of the 3 percent Cr and the 3 percent Cr 2 percent Re modified alloys were approximately the same as the as-cast tensile strengths; however, substantial increases in elongation were observed over the as-cast alloys. At 1800° F the elongations of these alloys in the as-cast condition were approximately 17 and 26 percent, as compared with approximately 35 percent for annealed sheet. At room temperature both alloys had tensile strengths above 210,000 psi and maximum elongations above 25 percent in the as-rolled condition.
- 5. Although the chromium content of these alloys was limited to 3 percent in order to reduce the amount of evaporative loss upon long time exposure (10,000 to 30,000 hr) to the space environment at elevated temperatures, the alloys are not subject to catastrophic oxidation in air at high temperatures. Their oxidation resistance was slightly better than

the strongest previously reported alloy in this series (Co-25W-1Ti-1Zr-0.4C) and considerably better than that of unalloyed cobalt. When coated with a commercial aluminum-iron diffusion coating, the oxidation in 300 hours of one of these alloys at 1900° F was negligible.

REFERENCES

- 1. Sykes, W. P.: The Cobalt-Tungsten System. Trans. Am. Soc. Steel Treating, vol. 21, 1933, pp. 385-423.
- 2. Adkins, E. F., Williams, D. N., and Jaffee, R. I.: Development of Wrought Cobalt-Tungsten-Base Alloys. Cobalt, no. 8, Sept. 1960, pp. 16-29.
- 3. Freche, John C., Ashbrook, R. L., and Klima, S. J.: A New Series of Cobalt-Base Alloys for Advanced Space Power Systems. Jour. of Metals, Dec. 1963, pp. 928-934.
- 4. Diedrich, James H., and Lieblein, Seymour: Materials Problems Associated with the Design of Radiators for Space Power Plants. In Section D, Power Systems for Space Flight. (Edited by Morris Zipkin and Russell N. Edwards). Progress in Astronautics and Aeronautics, vol. XI, Academic, 1963, pp. 627-653.
- 5. Scheuermann, C. H., Barrett, C. A., Lowdermilk, W. H., and Rosenblum, L.:

 Snap-8 Materials. Astronautics and Aerospace Engineering,

 Dec. 1963, pp. 40-43.
- 6. Dushman, Saul: Scientific Foundations of Vacuum Techniques. Second ed., Wiley, 1962.
- 7. Freche, John C., and Waters, William J.: Exploratory Investigation of Advanced-Temperature Nickel-Base Alloys. NASA MEMO 4-13-59E, 1959.

- 8. Freche, John C., Riley, Thomas J., and Waters, William J.: Continued Study of Advanced-Temperature Nickel-Base Alloys to Investigate Vanadium Additives. NASA TN D-260, 1960
- 9. Haynes Stellite Alloy No. 31. Union Carbide Stellite Co.
 Division Union Carbide Corporation, April 1958.
- 10. Morral, F. R., and Wagner, H. J.: Physical and Mechanical Properties of the Cobalt-Chromium-Tungsten Alloy WI-52. DMIC Memo 66, 1960.
- 11. High Temperature Cobalt Base Superalloy. Sierra Metals Data SM-302,
 Martin Metals Co., 250 N. 12th St., Wheeling, Ill.
- 12. High Temperature Cobalt Base Superalloy. Sierra Metals Data SM-322.

 Martin Metals Co.
- 13. Sierra Metals Data SM-200. Martin Metals Co.
- 14. Freche, John C., and Waters, William J.: Continued Investigation of an Advanced-Temperature Tantalum-Modified, Nickel-Base Alloy.

 NASA TN D-1531, 1963.
- 15. Wagner, H. J., and Hall, A. M.: The Physical Metallurgy of Cobalt-Base Superalloys. DMIC Memo 171, 1962.

TABLE I. - ALLOY COMPOSITIONS

(a) Alloys investigated

Alloy	Composition of random heats, weight percent						i
	Co	W	Ti	Zr	Cr	Re	С
Co-25W-lTi-0.4C	72.83	25.84	0.98				0.334
Co-25W-lTi-lZr-O.4C	Bal.	24.18	1.17	0.51			.42
Co+25W-lTi-lZr-lCr-0.4C	Bal.	24.89	0.98	•49	0.90		. 36
Co-25W-1Ti-1Zr-2Cr-0.4C	Bal.	24.08	. 94	•49	1.90		.37
Co-25W-lTi-lZr-3Cr-0.4C	70.12	24.82	. 88	•57	2.91		0.43
Co-25W-lTi-lZr-3Cr-lRe-0.4C							
Co-25W-lTi-lZr-3Cr-2Re-0.4C	Bal.	26.52	1.01	•56	3.06	2.07	.42
Co-25W-lTi-lZr-3Cr-2Re-0.4C	68.13	24.82	.93	•45	3.01	1.90	.44
Co-25W-1Ti-1Zr-3Cr-3Re-0.4C	Bal.	24.73	•97	. 48	2.85	2.72	-41

(b) Commercial alloysa

Alloy	Composition, weight percent										
	Co	Cr	Ni	W	Ср	Ta	Fe	Ti	В	Zr	C
WI-52	Bal.	21	may first	11	2		2				0.45
L-605	Bal.	20	10	15	11		1				•10
HS-31	Bal.	2 5	10	8	art 14		1.5				. 50
SM-302	Bal.	22		10		9			0.005	0.20	. 85
SM-322	Bal.	21.5		9		4.5	.7 5	0.75		2.25	1.0

^aData from refs. 10, 15, 9, 11, and 12 for WI-52, L-605, HS-31, SM-302, and SM-322, respectively.

TABLE II. - SUMMARY OF AS-CAST STRESS-RUPTURE DATA

A7.7	I	T	 	· · · · · ·
Alloy	Condition	Test temperature, o _F	Stress, psi	Life, hr
Co-25W-1Ti-1Zr-0.4C	Uncoated	1850	15,000	37.5 122 117.8
Co-25W-1Ti-1Zr-1Cr-0.4C	Uncoated	1850	15,000	82 101.5
Co-25W-1Ti-1Zr-2Cr-0.4C	Uncoated	1850	15,000	61.5 110.1
Co-25W-1T1-1Zr-3Cr-0.4C	Uncoated	1850	15,000	90.8 132.6 169.7 130.5
			20,000	14.5 20.5 17.6
e e			12,500	338.2 361.6
			10,000	816.2 723.1
		2000	20,000	0.9 .6
		·	15,000	4.7 12.3 7.0
			10,000	66.7 47.3
	Coated	2000	10,000	62.0
Co-25W-1TH-1Zr-5Cr-0.4C	Uncoated	1850	15,000	94.3 127.4 135.8 158.7

TABLE II. - CONCLUDED. SUMMARY OF AS-CAST STRESS-RUPTURE DATA

Alloy	Condition	Test temperature, or	Stress, psi	Life, hr
Co-25W-1Ti-1Zr-3Cr-1Re-0.4C	Uncoated	1850	15,000	136.2 158.4 130.1 106.0 95.8
Co-25W-1T1-1Zr-3Cr-2Re-0.4C	Uncoated	1850	15,000	213.9 208.7 185.1 134.7
			20,000	32.8 25.2
			10,000	1078.3 935.3
		2000	20,000	1.2
			15,000	8.3 10.2
			10,000	78.2 91.7 72.5
	Coated	2000	10,000	136.7
	Uncoated	2100	10,000 7,500 5,000	8.9 23.8 80.4
		2200	5,000	22.8
	Coated	2200	5,000	24.9
	Uncoated	2200	2,500	57.6
	Coated	2200	2,500	71.7
Co-25W-1Ti-1Zr-3Cr-3Re-0.4C	Uncoated	1850	15,000	183.8 170.4 154.1

(a) As-cast.

					. 1
Alloy	Test temperature, o _F	Yield strength, psi	Ultimate tensile strength, psi	Elonga- tion, percent	Reduction in area, percent
Co-25W-1Ti-1Zr-0.4C	Room temperature	77,500 82,500 86,400 79,000 79,980	91,200 100,000 103,000 99,100 99,600	5 4 4 1.5 3	5.8 2.3 3.2 2.3 3.8
Co-25W-1Ti-1Zr-3Cr-0.4C	Room temperature	83,200 74,800 79,750 76,700	96,500 94,100 98,000 97,100	2.5 3.7 2.2 2.5	3.1 3.1 3.0 2.3
	1645		61,000 65,000	4.0 4.5	
	1800	and the case and the	31,400 43,100 37,800	21 14 16.5	
	2000		24,300 23,700	32 ^a 17.5	
	204 5		21,800	28	
	2100		20,100 19,500	35 35	*******
Co-25W-1Ti-1Zr-3Cr-2Re-0.4C	Room temperature	80,400 82,500	96,700 99,400	2.1 2.5	2.3 3.1
·	1600		73,500	2.5	4 = 4
	1645		57,600	2.5	,a
	1800		35,500 35,900	24 28.5	
	2000		26,200 24,400	21 20	
	2045		24,100	25	
	2100		19,100 20,200	32 30	test tes

^aBroke outside gage length.

TABLE III. - CONCLUDED. SUMMARY OF TENSILE DATA

(b) Sheet

		-	 	· · · · · · · · · · · · · · · · · · ·		
Alloy	Condi tion	Test tempera- ture, o _F	Yield strength, psi	Ultimate tensile strength, psi	tion,	Reduction in area, percent
Co-25W-1Ti-1Zr-0.4C	As rolled	Room temper- ature	118,700 122,400 113,400	185,000 179,000 174,000	21.5 20 19	22.1 19.8 17.8
Co-25W-1Ti-1Zr-3Cr-0.4C	As rolled	Room temper- ature	168,000 179,100	226,800 216,200	19 25.5	13.7 29.2
	^a Annealed	Room temper- ature	110,700 102,000	170,300 177,200	17 23	16.3 18.1
		1600		69,300 7 3,000	7.5 7	4.6 6.1
		1800		36,600 37,600	37.2 34	39.9 36.1
Co-25W-1Ti-1Zr-3Cr-2Re-0.4C	As rolled	Room temper- ature	145,700 168,100	211,700 210,600	29.5 13	24.7 17.3
	^a Annealed	Room temper- ature	107,200	177,000 186,500	22.5 31	19.5 22.5
		1600		75,200 80,100	4.5 6	3.9 6.1
		1800		40,300 34,100	35.5 36	23.7 34.6

^a1/2 hr at 2350° F; water quench.

TABLE IV. - SUMMARY OF HARDNESS DATA

Alloy	Average Rockwell C hardness	Condition
Co-25W-lTi-lZr-lCr-0.4C	30. 5	As cast
Co-25W-lTi-lZr-2Cr-0.4C	32. 5	As cast
Co-25W-lTi-lZr-3Cr-0.4C	33.5 48.5 40	As cast As rolled Annealed
Co-25W-1Ti-1Zr-5Cr-0.4C	33	As cast
Co-25W-lTi-lZr-3Cr-lRe-0.4C	33	As cast
Co-25W-lTi-lZr-3Cr-2Re-0.4C	34.5 50.5 39	As cast As rolled Annealed
Co-25W-lTi-lZr-3Cr-3Re-0.4C	31.5	As cast

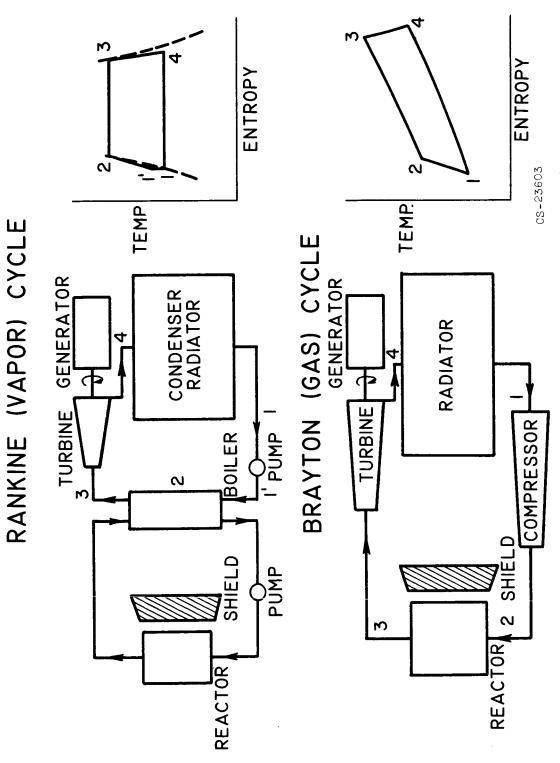


Figure 1. - Nuclear turbogenerator cycles (ref. 4).

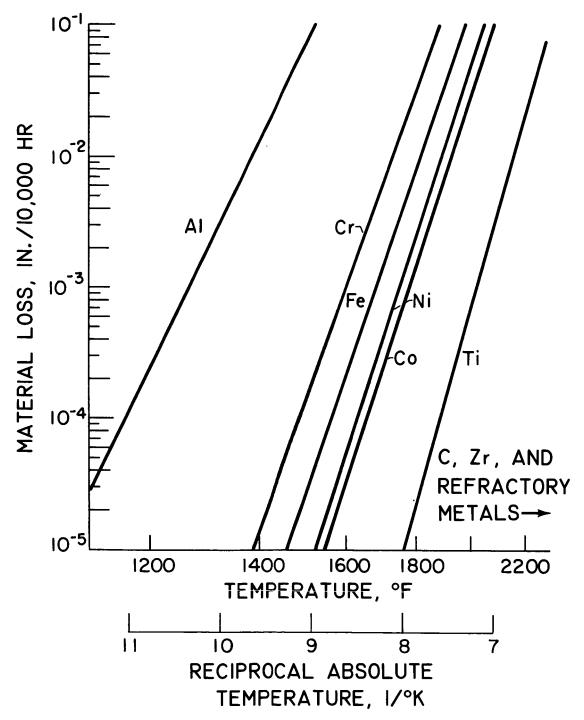
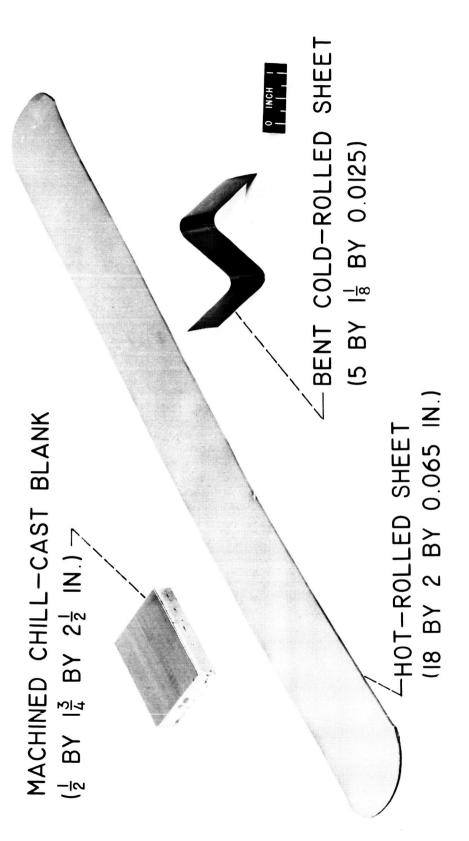
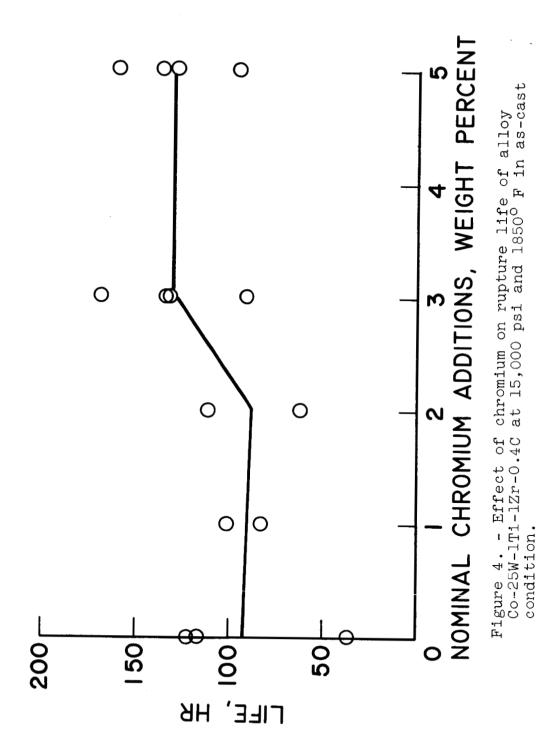


Figure 2. - Material loss in vacuum as function of temperature for several metals (ref. 6).



C-66229

Figure 3. - Alloy: Co-25W-lTi-1Zr-3Cr-2Re-0.4C.



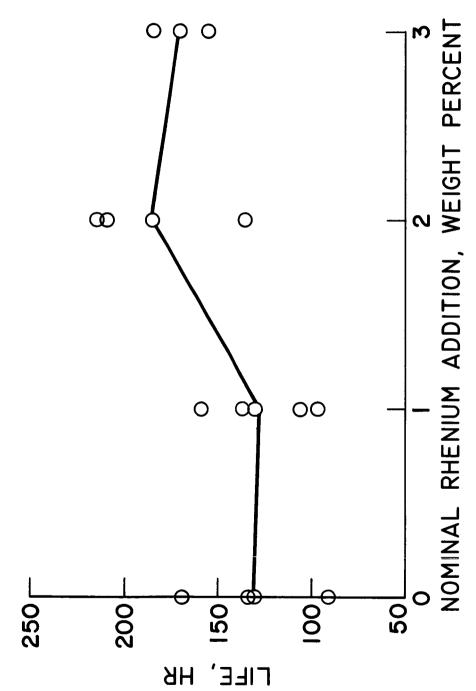


Figure 5. - Effect of rhenium additions on rupture life of alloy Co-25W-lTi-lZr-3Cr-0.4C at 15,000 psi and 1850° in as-cast condition.

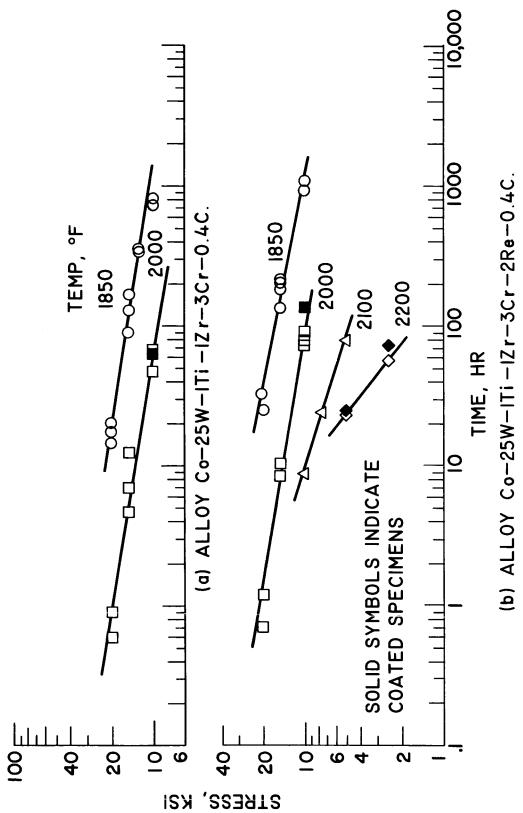


Figure 6. - Stress-rupture properties of chromium- and chromium-rhenium-modified cobalt-base alloys.

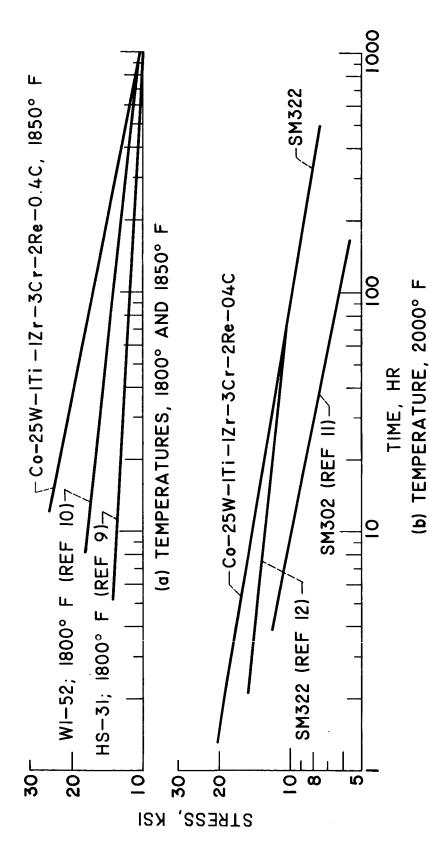


Figure 7. - Comparison of stress-rupture properties of alloy Co-25W-1Ti-1Zr-3Cr-2Re-0.4C with conventional cobalt-base alloys.

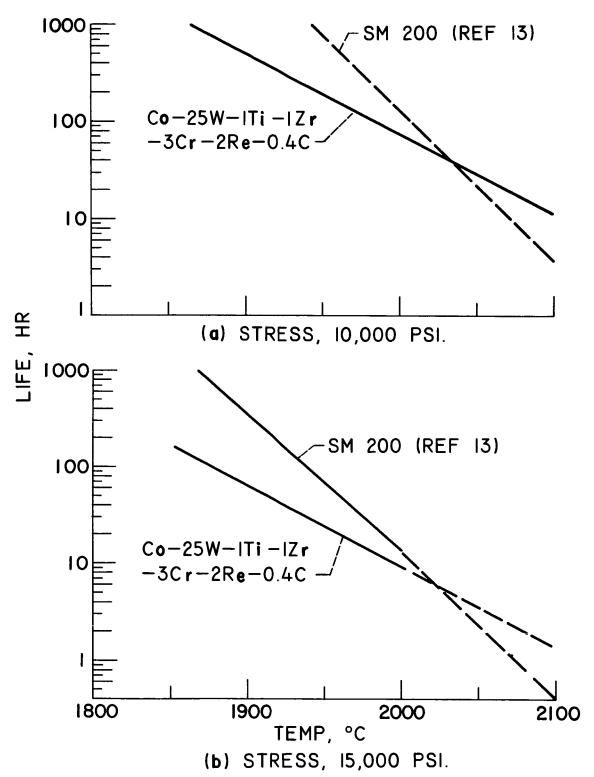


Figure 8. - Comparison of stress-rupture properties of alloy Co-25W-lTi-lZr-3Cr-2Re-0.4C with one of the strongest nickel base alloys, showing crossover at the higher temperatures.

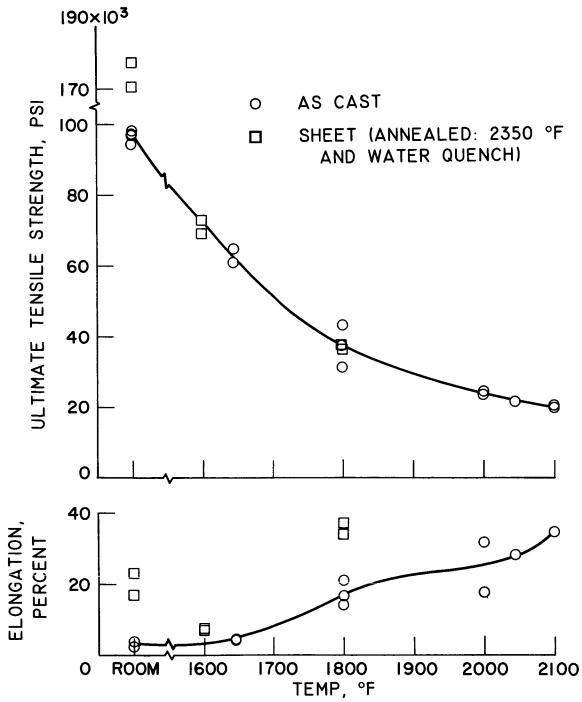


Figure 9. - Tensile properties of alloy ${\tt Co-25W-lTi-lZr-3Cr-0.4C}$ as function of test temperature.

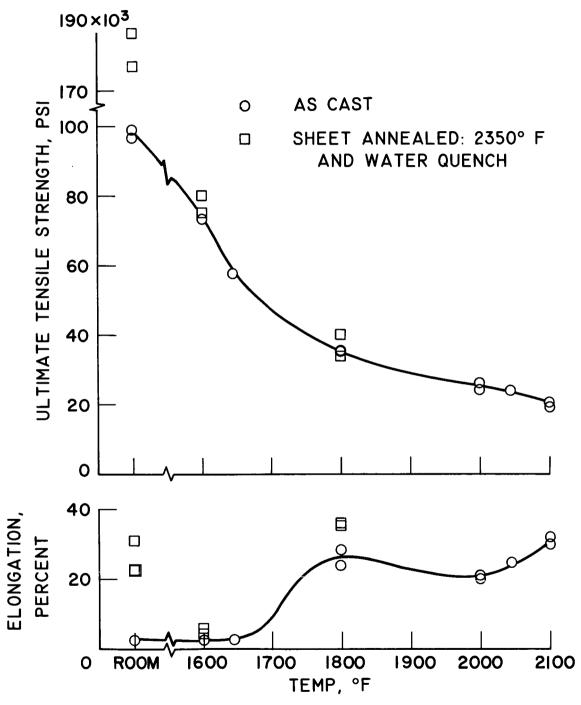


Figure 10. - Tensile properties of alloy Co-25W-lTi-lZr-3Cr-2Re-0.4C as function of temperature.

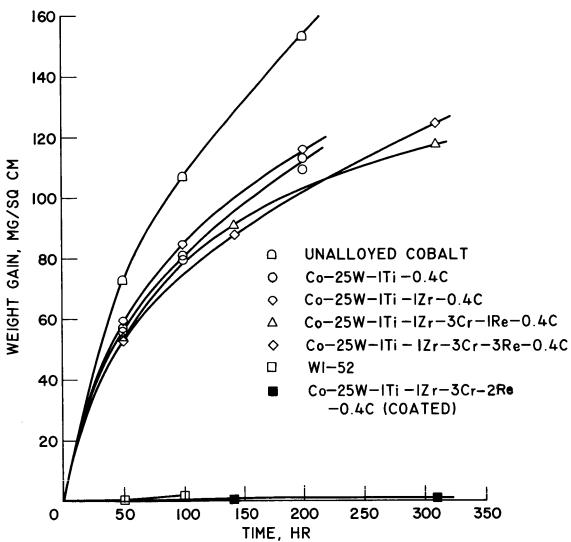
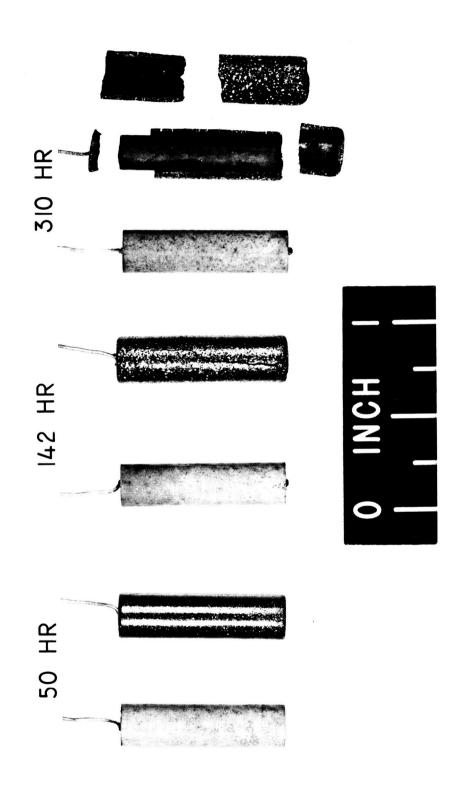
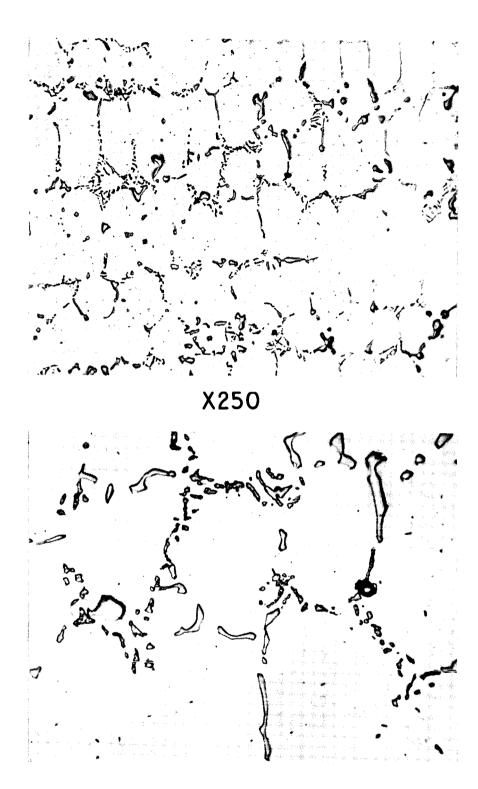


Figure 11. - Weight gain per unit area as function of time in air at 1900° F for unalloyed cobalt and several cobalt base alloys.



C-64903

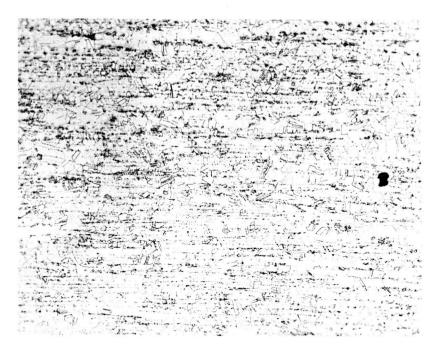
Figure 12. - Oxidation of coated and uncoated chromium-rhenium modified alloys at 1900° F in air for 50, 142, and 310 hours. Coated alloy: Co-25W-1Ti-1Zr-3Cr-2Re-0.4C. Uncoated alloy: Co-25W-1Ti-1Zr-3Cr-1Re-0.4C.



X750

(a) Alloy Co-25W-1Ti-1Zr-0.4C.

Figure 13. - As-cast microstructure of alloys.

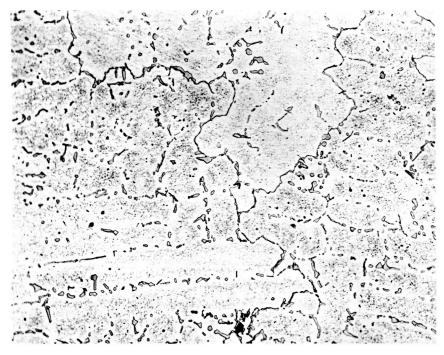


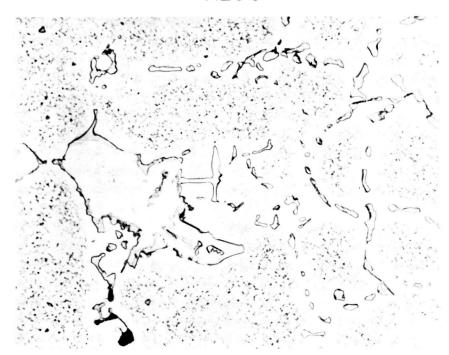


X750

(d) Alloy Co-25W-lTi-lZr-3Cr-2Re-0.4C sheet annealed at 2350 $^{\rm O}$ F for 30 minutes.

Figure 14. - Concluded. Microstructure of sheet material.

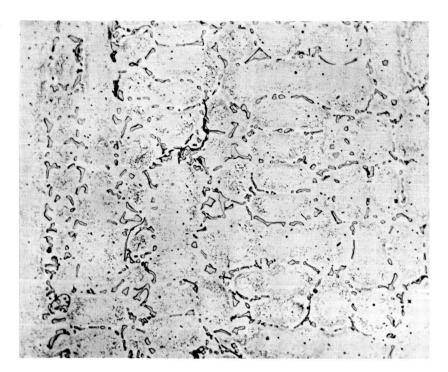


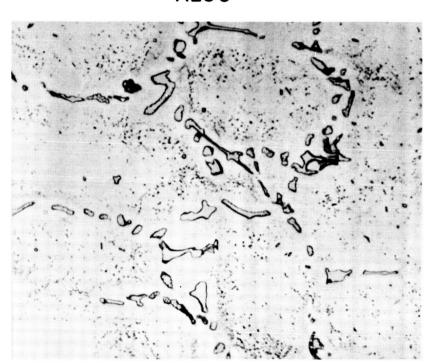


X750

(b) Alloy Co-25W-lTi-lZr-3Cr-0.4C.

Figure 13. - Continued. As cast microstructure of alloys.

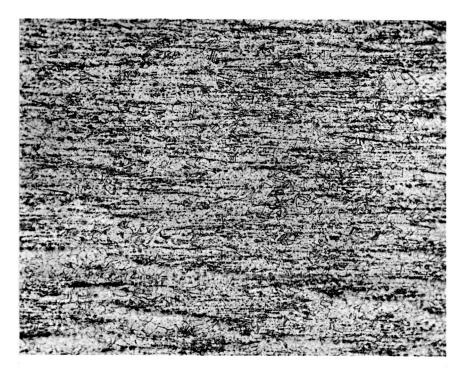




X750

(c) Alloy Co-25W-lTi-1Zr-3Cr-2Re-0.4C.

Figure 13. - Concluded. As-cast microstructure of alloys.

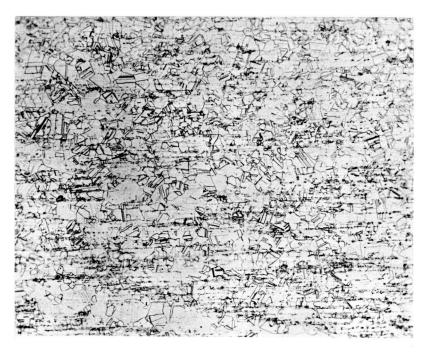


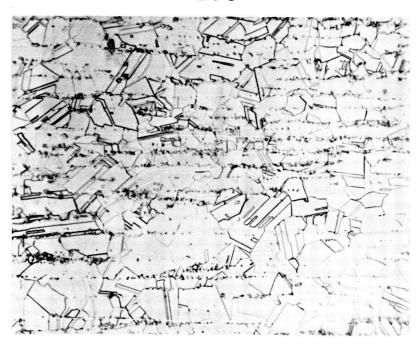
X250



X750

(a) Alloy Co-25W-lTi-lZr-3Cr-0.4C as hot-rolled. Figure 14. - Microstructure of sheet material.

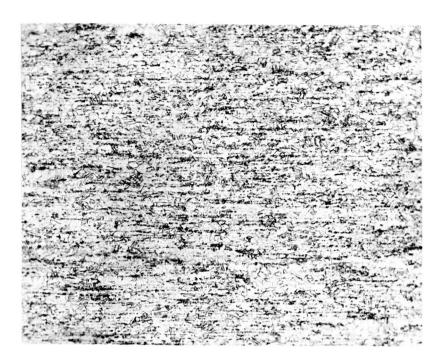




X750

(b) Alloy Co-25W-lTi-lZr-3Cr-0.4C sheet annealed at 2350° F for 30 minutes.

Figure 14. - Continued. Microstructure of sheet material.





X750

(c) Alloy Co-25W-lTi-lZr-3Cr-2Re-0.4C as hot-rolled.

Figure 14. - Continued. Microstructure of sheet material.